

**Gravatt, Dan**

---

**From:** Gravatt, Dan  
**Sent:** Thursday, April 25, 2013 9:10 AM  
**To:** Ammon, Doug; Bartenfelder, David; openchowski, charles; Wilhelm, Ron; Walker, Stuart  
**Cc:** Asher, Audrey; Singletary, DeAndre; Tapia, Cecilia  
**Subject:** West Lake Landfill: SOW for Fate and Transport Modeling (sixth and final SSFS workplan)  
**Attachments:** FT Modeling SOW 4-22-2013.pdf

Doug, Dave, Charles, Ron and Stuart:

Attached is the sixth and final workplan for the West Lake Supplemental SFS analyses requested by the National Remedy Review Board. The first four were sent to you (through Amy Legare) in an e-mail dated November 15, 2012, and the fifth was sent directly to you in an e-mail dated February 5, 2013.

It is my understanding that you have been tasked to review these workplans for compliance with the NRRB's comments/requests on Region 7's "early consultation" presentation on the SFS report, in lieu of a review by the NRRB itself as I originally requested. In a conference call with you on January 9, 2013, you indicated that you would not provide comments on any of the six SSFS workplans until you had all six of them to review.

You now have all six workplans that comprise the scope of the SSFS as defined in the Region's letter to the OU1 PRPs of October 12, 2012. I request that you provide me your comments on these six workplans by Friday, May 10, 2013. If you have any questions or need me to re-send the earlier workplans, let me know ASAP.

Sincerely,  
Daniel R. Gravatt, PG  
US EPA Region 7 SUPR/MOKS  
11201 Renner Boulevard, Lenexa, KS 66219  
Phone (913)-551-7324

Principles and integrity are expensive, but they are among the very few things worth having.

---

**From:** Paul Rosasco [mailto:paulrosasco@emsidenver.com]  
**Sent:** Monday, April 22, 2013 10:37 AM  
**To:** Gravatt, Dan; 'Muenks, Shawn'  
**Cc:** 'Merrigan, Jessie (LG)'; 'Charlotte L. Neitzel'; 'Whitby, Kathleen'; 'Warren, Victoria'; steven.golian@em.doe.gov; 'Matt'  
**Subject:** SOW for Fate and Transport Modeling

Attached is a Statement of Work for Fate and Transport Modeling for West Lake Landfill OU-1.

0714



3.0

## **Scope of Work and Schedule**

### **Fate and Transport Modeling**

#### **Introduction**

The U.S. EPA's October 12, 2012 letter (USEPA, 2012) requested that the Respondents perform fate and transport modeling at the West Lake Landfill (the Site). This Scope of Work (SOW) describes the modeling approach proposed to estimate potential fluxes of landfill leachate, possible radionuclide concentrations within the leachate, and the potential for transport of any radionuclide-contaminated leachate within the subsurface.

This SOW first outlines the objectives of the proposed modeling task. This is followed by a discussion of the general conceptual site model (CSM). Features of the Site that are expected to be simulated are described together with potential events and the physical and chemical transport processes that are envisioned as being incorporated in the modeling analyses. After describing the CSM and defining the objectives of the modeling calculations - which together define the necessary capabilities of the developed model - the calculation approach and the simulation programs proposed to meet the modeling objectives are identified. The final suite of scenarios to be simulated will be determined as part of the model implementation task.

It is assumed that modeling calculations will be performed on the basis of existing site-specific data, augmented where necessary with information and values obtained from technical literature and/or derived from professional experience.

#### **Background**

West Lake Landfill is located within the western portion of the St. Louis metropolitan area approximately two miles east of the Missouri River. Two areas of the Site contain radionuclides as a result of the use of soils mixed with leached barium sulfate residue as cover for municipal refuse. The Site is divided into two Operable Units (OUs). OU-1 consists of the two areas within the landfill where radionuclides are present and the area formerly described as the Ford Property, now called the Buffer Zone/Crossroad Property. OU-2 consists of other landfill areas that are not impacted by radionuclides (USEPA, 2008). Modeling calculations proposed in this SOW address the potential fate of radionuclides within OU-1. The nature and extent of radionuclides within OU-1 are discussed in the Remedial Investigation (EMSI, 2000) and a Supplemental Feasibility Study (SFS) (EMSI, 2011) for OU-1.

The selected remedy for OU-1 presented in the Record of Decision (ROD) includes source control through containment of waste materials and institutional controls for the landfilled waste materials (USEPA, 2008). Components of the ROD-selected remedy include the following:

1. A new landfill cover over the existing surface of Areas 1 and 2;
2. Consolidation of radiologically contaminated surface soil from the Buffer Zone/Crossroad Property to the containment area;
3. Groundwater monitoring and protection standards consistent with requirements for uranium mill tailing sites and sanitary landfills;
4. Surface water runoff control;
5. Gas monitoring and control including radon and decomposition gas as necessary;
6. Institutional controls; and
7. Long-term surveillance and maintenance of the remedy.

Performance standards for these remedy components are detailed in the ROD. The following additional performance standards were also identified for the OU-1 remedy (EMSI, 2011):

- The proposed cap should meet the Uranium Mill Tailings Radiation Control Act of 1978 (UMTRCA) guidance for a 1,000-year design period including an additional thickness to prevent radiation emissions;
- Air monitoring stations for radioactive materials should be installed at both on-site and off-site locations;
- Groundwater monitoring should be implemented at the waste management unit boundary and at off-site locations; and
- Flood control measures at the Site should meet or exceed design standards for a 500-year storm event under the assumption that the existing levee system is breached.

As defined in the OU-1 ROD, the new landfill cover for Areas 1 and 2 would consist of the following, from bottom to top: 2-ft of rock consisting of well-graded pit run rock and/or concrete/asphaltic rubble ranging from sand-sized up to 8-inches; 2-ft of compacted clay or silt that when compacted at optimum moisture content possesses a coefficient of permeability of  $1 \times 10^{-5}$  cm/sec or less; and 1-ft of soil suitable of supporting vegetative growth. These layer thicknesses are based on requirements of the Missouri Solid Waste Rules and the description of the cover system in the ROD (USEPA, 2008). [A separate task will evaluate potential alternative landfill cover designs including possible use of an Evapotranspiration (ET) cover or incorporation of a geomembrane into the design of the ROD-selected landfill cover.]

### **Modeling Objectives**

The proposed fate-and-transport modeling will provide site-specific calculations of the potential for radionuclides to leach from the landfill, reach the underlying saturated aquifer, and result in unacceptable concentrations within groundwater or surface water downgradient of the landfill. The following modeling objectives are proposed:

1. Calculate the potential for migration of leachate containing radionuclides from waste materials:
  - a. Under current conditions, to validate the modeling approach and potentially bound parameter values for later predictive analyses;

- b. Under future conditions, assuming the emplacement of a new landfill cover for OU-1; and
  - c. Under future conditions, following the period of active maintenance of the new landfill cover for OU-1.
- 2. Calculate the potential for leachate containing radionuclides to migrate vertically through waste that is uncontaminated by radiological constituents and through native materials beneath the landfill, and to impact underlying groundwater;

*If the prior calculations indicate that a potentially measurable impact to groundwater may occur:*

- 3. Calculate the likely fate of any radionuclides that reach groundwater, and the potential for the development of a contaminant plume;
- 4. Calculate concentrations over time of radionuclides in groundwater at defined locations including, but not limited to, the property fence line/boundary; and
- 5. Evaluate the potential for radionuclides that reach the groundwater to migrate toward, and discharge to, the Missouri River at levels exceeding standards.

These are the specific objectives of the proposed modeling task. The model may, at some later time, be used to support other Site objectives such as (a) designing a suitable groundwater monitoring program, including defining the locations and frequency of sampling to detect any potential off-site migration of radionuclide constituents and/or (b) evaluating alternative landfill cover designs such as an ET cover or incorporation of a geomembrane.

#### **Fate and Transport Conceptual Site Model**

Because the overall mass of radium at the Site is small<sup>1</sup> and future infiltration through the landfill materials will be less than at present due to the planned emplacement of an additional landfill cover over the existing landfill cover material, it might be expected that concentrations of radium will necessarily decline in the future. However, site-specific conditions need to be evaluated before reaching this conclusion. For example, uranium and thorium that are present in the waste materials will continue to decay, and in doing so, generate radium. In addition, the landfill and groundwater geochemistry will change over time due to the eventual exhaustion of readily-biodegradable organic matter in the landfill. This will in turn affect the stability of some minerals available to sequester radium.

Selection of an appropriate calculation method, and of a suitable simulation code or suite of codes to implement the calculations, requires that the modeling requirements are defined. In the context of radionuclides, the Nuclear Energy Agency Organization for Economic Co-operation and Development (NEA-OECD, 2000) developed a systematic approach to define relevant scenarios for safety assessment studies at radioactive waste management sites. This consists of identifying and prioritizing the Features,

---

<sup>1</sup> Using the arithmetic mean concentrations (reported as pCi/gram) from Appendix A of the RI, as well as an estimated mass of soils for the Area 1 and 2 surface and subsurface zones at the West Lake site, a preliminary estimate of the amount of <sup>226</sup>Ra at the site indicates that there is less than 40 grams of <sup>226</sup>Ra within Areas 1 and 2.

Events, and Processes (FEPs<sup>2</sup>) that potentially affect the fate and transport of radionuclides at a site, and developing and modeling individual scenarios, each of which consists of a well-defined, connected sequence of selected FEPs. This SOW identifies principal FEPs for the Site that it is anticipated will require consideration in the modeling analyses. However, the final site-specific FEPs and the suite of simulation scenarios will be defined during the implementation phase of the modeling task.

#### Primary Site-Specific Features

An overview of the primary features that affect radionuclide fate and transport is provided here. The source of radionuclides of potential concern is leached barium sulfate residue mixed with soil and used as daily and intermediate cover for municipal solid waste deposited in landfill Areas 1 and 2. This radiologically-impacted material (RIM) is currently covered by old landfill cover material. Underlying the RIM is refuse that does not contain radionuclides, and under that is partially saturated alluvium. Over time some fraction of radionuclide-bearing water could potentially percolate vertically to reach the water table. According to the RI [EMSI, 2000], the saturated aquifer largely consists of alluvial sand, underlain by more impervious limestone and dolomite bedrock. The horizontal hydraulic gradient within the aquifer is relatively flat, which would tend to result in slow advection along a trajectory that intersects the Missouri River downgradient of the Site. If radionuclide-containing water currently located within or under OU-1 were to reach the water table beneath the landfill, then mixing, dispersion, and dilution of that radionuclide-containing water would occur at the water table beneath the landfill, within the saturated aquifer, and within the hyporheic zone of the Missouri River.

A dominant feature [which, depending upon the simulation scenario, may also constitute an event] that must be considered in the modeling calculations, and for which a design is presented in the ROD but for which potential alternatives have since been identified by USEPA for evaluation, is the new landfill cover to be installed over the current surface of the old landfill cover. Modeling calculations proposed under this SOW will only consider the ROD-selected landfill cover, the design of which is detailed above and within the ROD (USEPA, 2008). However, the developed model could be used at some later time to evaluate alternative cover designs such as an ET cap and/or the incorporation of a geomembrane within the ROD-selected landfill cover.

#### Primary Site-Specific Events

Several events may affect the landfill water balance, the potential for radionuclide partitioning and migration, and the potential for radionuclide transport within the partially saturated and saturated zones at the Site. Example events are summarized in Table 1.

---

<sup>2</sup> The following definitions apply (Sandia National Laboratories, 2010):

*Feature* – An object, structure, or condition that has a potential to affect repository system performance.

*Event* – A natural or human-caused phenomenon that has a potential to affect repository system performance and that occurs during an interval that is short compared to the period of performance.

*Process* – A natural or human-caused phenomenon that has a potential to affect repository system performance and that occurs during all or a significant part of the period of performance.

**Table 1 Primary Events and Processes of Potential Radionuclide Fate and Transport at the Site.**

FEP Element	Description
<b>Events:</b>	<ol style="list-style-type: none"> <li>1. Transition from current cover conditions to final cover under active maintenance: <ul style="list-style-type: none"> <li>• Cover design (2-ft of well-graded pit run rock and/or concrete/asphaltic rubble; 2-ft of compacted clay or silt with a coefficient of permeability of <math>1 \times 10^{-5}</math> cm/sec or less; and 1-ft of soil suitable of supporting vegetative growth)</li> <li>• Period of active maintenance (30 yr min/200 yr ROD/1000 yr UMTRA-compliant)</li> </ul> </li> <li>2. Transition from active maintenance period to post-active maintenance period: <ul style="list-style-type: none"> <li>• Intermediate infiltration rates (reduced by grade, vegetation, etc.)</li> </ul> </li> <li>3. [Bio-]degradation of landfill wastes: <ul style="list-style-type: none"> <li>• Degradation time-frame (rapid versus extended time)</li> <li>• Effects and duration on chemistry (oxidation-reduction [redox], carbonate, CO<sub>2</sub>, pH, etc.)</li> </ul> </li> <li>4. Flood events: <ul style="list-style-type: none"> <li>• 500 year</li> </ul> </li> </ol>
<b>Processes:</b>	<ol style="list-style-type: none"> <li>1. Net infiltration: <ul style="list-style-type: none"> <li>• Under current conditions</li> <li>• During period of active cover maintenance (incorporating ET as a process)</li> <li>• Following period of active cover maintenance (reduced by grade, vegetation, etc.)</li> </ul> </li> <li>2. Ingrowth of radium from uranium and thorium decay:</li> <li>3. Partitioning of radium, uranium, thorium from soil to water/landfill leachate: <ul style="list-style-type: none"> <li>• Decay/ingrowth, sorption/complexation, mineral dissolution/precipitation</li> </ul> </li> <li>4. Transport within the partially-saturated zone:</li> <li>5. Mixing at the water table: <ul style="list-style-type: none"> <li>• Depth of penetration, and dilution</li> <li>• Sorption/complexation, mineral dissolution/precipitation</li> </ul> </li> <li>6. Transport within the saturated aquifer: <ul style="list-style-type: none"> <li>• Advection, dispersion, decay/ingrowth, sorption/complexation, mineral dissolution/precipitation</li> </ul> </li> <li>7. Discharge to, and mixing with, Missouri River: <ul style="list-style-type: none"> <li>• Hyporheic zone chemical process</li> <li>• Sorption/complexation, mineral dissolution/precipitation</li> </ul> </li> </ol>

*The Uranium Mill Tailings Remediation Program (UMTRA) focused on the design of purpose-built repositories for uranium tailings piles; however, the UMTRA containment design time-frame of 1000 years is a guide for other radionuclide wastes.*

One important event is the grading of Areas 1 and 2 and the emplacement of the final landfill cover on top of the current landfill cover material in these areas. This new cover will greatly reduce infiltration and the potential for mass transfer of radionuclides to mobile water for the period of active maintenance. If active maintenance were to cease, over some time the effectiveness of the landfill cover may decline, potentially resulting in an increased infiltration rate. However, infiltration rates following cessation of active cover maintenance would be expected to be lower than under current

conditions since the cover design incorporates a grade (whereas, the majority of the current landfill cover is flat) and other features that would endure for many years following cessation of active maintenance.

Another important event is the slowing rate of biodegradation of organic materials in the landfill over time; this will alter the geochemistry within the landfill wastes and impact radionuclide partitioning between mobile and immobile phases in the refuse that contains RIM, the underlying refuse that does not contain RIM, and potentially the underlying alluvial aquifer.

#### Primary Site-Specific Processes

Several processes may affect the potential for radionuclide partitioning and migration, and the potential for radionuclide transport within the partially saturated and saturated zones at the Site. Example processes are summarized in Table 1. One important process is the complex interaction of the RIM with the surrounding pore water, and the role of pore water and soil chemistry on the potential for radionuclide partitioning and migration. Since radionuclide geochemistry will be an important process in the modeling scenarios, an overview of relevant radionuclide geochemistry is provided below.

### **Geochemistry of Radionuclide Decay, Ingrowth, Partitioning and Migration**

#### Radium Geochemistry

Radium dominantly occurs within leached barium sulfate residues that were mixed with soil and used as daily and intermediate soil cover for solid waste disposed at Areas 1 and 2. The co-precipitation of radium into barium sulfate is a well known process to control radium (Doerner and Hoskins, 1925; Bruno et al., 2007; Zhu 2004a, 2004b; Mahoney 1998, 2001; Grandia et al., 2008; Bosbach et al., 2010). Consequently, equilibrium between pore water and the radium component of barium sulfate will define the initial radium source term leached from the RIM.

Radium may also be attenuated in clean alluvium and groundwater via adsorption onto iron-bearing minerals, ion exchange on clays, and co-precipitation with other sulfate and carbonate minerals such as gypsum and calcite. Of these mechanisms, co-precipitation is expected to be the dominant process close to the landfill due to the sandy nature of the aquifer and expectedly low redox conditions (making iron oxyhydroxides unstable). Downgradient of the landfill - and increasingly within the landfill over time - more oxidizing conditions may be present, and the abundance of iron-bearing minerals available for radium adsorption may increase. Another important consequence of the change in landfill biogeochemistry over time is the likely increase in pH as readily-biodegradable material is consumed. As pH increases, the amount of calcite that will precipitate will increase, and radium co-precipitation with calcite will be more favored, reducing its mobility.

#### Uranium Geochemistry

Uranium and thorium are important because they occur within the RIM and they decay over time, producing additional radium. Under current conditions uranium concentrations are expected to be controlled by uraninite ( $\text{UO}_2$ ) due to the reducing conditions within the landfill. If oxidizing conditions

return, however, then uranium solubility could be controlled by the generally more soluble  $U^{+6}$  (uranyl) minerals such as schoepite  $[UO_2(OH)_2 \cdot 2H_2O]$  or less soluble forms such as carnotite  $(KUO_2VO_4)$  and tyuyamunite  $[Ca(UO_2)_2(VO_4)_2]$  (Tokunaga et al., 2009). In addition to the oxidation state of uranium, other factors affecting dissolved concentrations include levels of dissolved carbonate generated by biodegradation (which increase solubility) and presence of iron oxyhydroxides (which decrease solubility).

### Thorium Geochemistry

Thorium is not redox sensitive and solubility conditions will be controlled by thorianite ( $ThO_2$ ) under all redox conditions. Complexation reactions that form thorium carbonate complexes are not as significant as those for uranyl carbonate complexes, but they will play a role in thorianite solubility calculations. Reductions in carbon dioxide pressures will also reduce thorium concentrations in groundwater.

The long-term in-growth of  $^{226}Ra$  from  $^{230}Th$  is complicated by the fact that the majority of in-growth radium will be retained within the crystal structure of the thorianite ( $ThO_2$ ). Only a small fraction of the radium that is produced from the decay of thorium will have the potential to be released to groundwater. This fraction is expected to be derived from near the surface of the thorianite crystals.

### **Calculation Approach**

#### General

The approach to undertaking modeling calculations will follow the sequence of steps defined below:

- Determine and document final FEPs;
- Identify simulation scenarios, based on the final FEPs;
- Identify parameter ranges and uncertainties;
- Develop necessary model(s);
- Complete model calculations; and
- Present and interpret results.

As the modeling is implemented, there will be some iteration between steps in the sequence. It is expected that there will be communication and interaction with USEPA to seek input on the FEPs, simulation scenarios, and parameter ranges and uncertainties identified for inclusion in the modeling prior to undertaking the model calculations. It is envisioned that communication and interaction will include the following:

- Presentation and discussion of certain detailed or fundamental concepts – such as the CSM, FEPs and scenarios for inclusion in the modeling;
- Discussion of other less critical aspects of the modeling task; and
- Presentation of intermediate deliverables for review and discussion.



### Graded Approach

A graded approach is proposed to undertake the modeling analyses (USEPA 2002, 2009). This graded approach will:

- Use relatively simple methods for initial calculations under the premise that the inherent conservatism is protective of groundwater and other receptors. Increasing simulation rigor will only be used, if necessary, if simpler approach(es) yield unreasonable results.
- Provide a mechanism to cease model calculations if it becomes evident that no further calculations are necessary. For example, saturated zone flow and transport calculations will only be undertaken if geochemical and vadose zone modeling calculations suggest that a potentially measurable impact to groundwater could occur.

The modeling approach and specific model calculations will be designed to incorporate the principal FEPs while mitigating the potential for computationally-intensive calculations that prevent a thorough exploration of parameter variability and scenario uncertainty. Multiple scenarios will be simulated to evaluate the potential impact of scenario uncertainty on model outcomes, while sensitivity analysis will be used to evaluate the potential impact of parameter variability on model outcomes.

Modeling analyses will be designed to predict the concentration of radium in groundwater for a period of 1,000 years. Concentrations will be forecast at defined compliance locations including, but not limited to, the property fence line/boundary, for the 1,000-year period and will be compared to regulatory standards. If regulatory standards are not exceeded then no further analyses will be required. However, if simulated concentrations exceed regulatory standards, the graded approach will be used to identify the technical element of the modeling approach that incurs the most inherent conservatism in the calculations so that element of the modeling approach can be treated more rigorously to reduce that inherent conservatism (Dixon et al, 2008). If the graded simulation approach has been applied until all inherent conservatisms have been reduced or eliminated, yet simulated concentrations exceed regulatory standards, then this will be considered to be a reliable result.

### Simulation Code Selection

Table 1 outlines primary events and processes that will be considered in the calculations. The range of potential outcomes will be evaluated by performing several model simulations that consider reasonable alternate conceptualizations of subsurface conditions. Since parameterization of the geochemical component of the model is likely subject to more variability and uncertainty than the groundwater flow component of the model - given the large number of chemical processes that potentially affect radium fate and transport - advective-dispersive migration will be simulated as one-dimensional (1-D), coupled with a rigorous treatment of the complex geochemical processes. The following sequential series of calculations is proposed to collectively comprise the model [consistent with the graded approach, some calculations will only be undertaken if necessary based on the results of preceding calculations]:

1. The Hydrologic Evaluation of Landfill Performance (HELP) code will be used to determine the run-off component of the surface-water balance and remaining water available for infiltration through cover materials under current conditions, final cover conditions, and following the period of active cover maintenance;
2. HYDRUS 1-D (Simunek et al., 1998) will be used to simulate the water balance in the subsurface (after run-off has been accounted for) and the migration of infiltrating water;
3. The USGS-supported geochemical simulation software, PHREEQC (Parkhurst and Appelo, 1999), which is linked to HYDRUS through the HP1 program (Jacques and Simunek, 2005), will be executed simultaneously to provide concentrations of radionuclides in the leachate as it moves within the unsaturated refuse and underlying unsaturated alluvium;
4. The depth of penetration of any leachate that reaches the water table will be calculated using an established method such as that detailed by USEPA (1996);
5. PHREEQC, linked with HYDRUS, will then be used to calculate the effects of mixing on geochemistry that occurs between the leachate and groundwater at the water table;
6. Output from these calculations will provide the time-varying groundwater composition for simulating 1-D radionuclide fate and transport within the saturated zone toward the Missouri River using PHREEQC; and
7. PHREEQC will be used to represent geochemical processes that may occur within the hyporheic zone of the Missouri River.

#### Overview of HELP Calculations

HELP (Schroeder, P.R. et al, 1994a, 1994b; Berger, 2011; Berger and Schroeder, 2012) is a program originally developed by USEPA to evaluate the effectiveness of landfill cover designs. HELP will first be used to estimate the typical, quasi-steady-state surface-water balance, emphasizing the run-off rate and the net water available for infiltration through the current landfill cover. The purpose of these calculations is solely to support validation of the modeling approach and constrain the values of certain parameters to be consistent with historical water samples. HELP will then be used to make similar calculations to estimate run-off and the net water available for infiltration through the new landfill cover that would be constructed under the ROD-selected remedy, and to estimate run-off and the net water available for infiltration through the new cover following the period of active maintenance. Alternate periods of active maintenance may be considered in alternate simulation scenarios. The HELP model can explicitly account for rainfall-runoff under alternate cover designs, including alternate slopes (grades).

#### Overview of HYDRUS 1-D Calculations

HYDRUS-1D (Simunek et al., 1998) is a public domain Windows-based modeling environment that simulates the movement of water, heat, and multiple solutes in variably saturated media. The flow equation formulation in HYDRUS incorporates a sink term to account for water uptake by plant roots, as well as a dual-porosity type flow capability in which one fraction of the water content is mobile and another fraction is immobile. The solute transport equations consider advective-dispersive transport in the liquid phase, as well as diffusion in the gaseous phase. HYDRUS 1-D (Simunek et al., 1998) will be

used to simulate the water balance in the subsurface (after run-off has been accounted for), and the migration of infiltrating water.

HYDRUS 1-D is linked to PHREEQC through the HP1 modeling software (Jacques and Simunek, 2005). This allows simulation of complex bio-geochemical reactions. Consistent with the graded modeling approach, the initial simulations will assume that radionuclide attenuation in landfill leachate only occurs in groundwater. However, the HP1 software may be used to estimate attenuation in the non-radiologically impacted refuse and unsaturated alluvium underlying Areas 1 and 2 if unreasonable results are obtained using the more conservative simplifying assumption.

#### Overview of PHREEQC Calculations

Geochemical modeling will first be completed to estimate the leaching potential of various radionuclides under current site conditions. The purpose of these calculations is to support validation of the groundwater modeling approach and constrain the values of certain parameters to be consistent with historical water samples. Following these calculations, the modeling will be used to evaluate the leaching potential under long-term future conditions under the ROD-selected remedy.

Geochemical modeling methods to estimate source term concentrations for the radio-isotopes will primarily rely upon equilibrium thermodynamics and will be based upon mineral solubility relationships using current ground water compositions. Calculations will be performed using PHREEQC (Parkhurst and Apello, 1999). Solubility calculations for end member phases will be used for thorium and uranium. Radium will be assumed to be present as a solid-solution in barite with a lower thermodynamic activity. Solubility constants for uranium and thorium will, for the most part, be based upon the OECD NEA compilations (Guillaumont et al., 2003; and Rand et al., 2008). Other data sources will be used as needed (Dong and Brooks, 2006, 2008; Duro et al., 2006; Langmuir, 1978; Tokunaga et al., 2009). The ingrowth of  $^{226}\text{Ra}$  from  $^{230}\text{Th}$  is a time dependent process and the kinetics capabilities in PHREEQC will be used to estimate the production of  $^{226}\text{Ra}$  for a period of 1,000 years.

1-D transport modeling will also be performed with PHREEQC. Modeling will simulate a chemical system that is sufficiently complex to include the effects of landfill and groundwater geochemistry described above. Site-specific groundwater and soil data for uranium, thorium, and radium will define initial concentrations for these isotopes. The site analytical results, particularly the groundwater analyses, will also provide details on the overall geochemical environment of the landfill. The PHREEQC fate and transport model will include the following features:

- The effect of radium in-growth from the decay of thorium over time;
- Decreased methane generation and a possible change in site redox conditions from the reducing conditions currently present at the site to more oxidizing conditions;
- Radionuclide precipitation and/or co-precipitation, such as the partitioning of radium into calcite (Yoshida et al., 2008) present within the landfill;
- Changes in iron stability and potential precipitation of iron-bearing phases for the adsorption of radionuclides; and

- Adsorption reactions (surface complexation and ion exchange) (Dzombak and Morel, 1990; Mahoney et al. 2009a, b; Rojo, et al., 2008; Pabalan et al., 1998).

### Model Validation and Predictive Sensitivity Analysis

Historical groundwater data have exhibited few detections of radionuclides. As such, a rigorous calibration exercise is not warranted or justifiable. However, the historical data will be used to validate the modeling calculations and potentially bound the values of some parameter combinations by simulating current conditions prior to undertaking predictive calculations. Multiple simulations will be conducted to evaluate the range of forecasts of possible impacts on groundwater beneath the landfill, at the property fence line/boundary, within surface water, at any defined receptors, and at any other locations of interest. Multiple scenarios will be simulated and predictive sensitivity analyses will be used to evaluate the potential impact of parameter variability on model outcomes at these locations. Although outside the scope of the proposed modeling task, the results of multiple-scenario and parameter-/prediction-sensitivity analyses can help guide the sampling frequency for long-term monitoring programs by providing a range of possible arrival-times and peak-concentrations for contamination at identified compliance locations such as the property fence line/boundary.

### **Deliverables**

The final deliverable anticipated to be developed from the modeling effort is a Technical Memorandum documenting the technical approach, assumptions, model development, parameterization, simulated scenarios, and results obtained. However, it is anticipated that there will be communication and interaction with USEPA to seek input on the FEPs, simulation scenarios, and parameter ranges and uncertainties identified for inclusion in the modeling prior to undertaking the model calculations. Communication and interaction with USEPA will include the following:

- Presentation and discussion of certain detailed or fundamental concepts – such as the CSM, FEPs and scenarios for inclusion in the modeling;
- Discussion of other less critical aspects of the modeling task; and
- Presentation of intermediate deliverables to USEPA for review and discussion.

No revisions to the SFS report are expected to be required as a result of this modeling effort.

### **Schedule**

It is anticipated that the geochemical evaluation of potential leaching of radionuclides, including preparation and submittal of the Technical Memorandum, will be completed within twelve weeks of the approval to proceed.

### **References**

Berger, K., 2011. The Hydrologic Evaluation of Landfill Performance (HELP) Model. Engineering Documentation for HELP 3.90 D - Enhancements Compared to HELP 3.07. Institute of Soil Science, University of Hamburg, Germany, 10 pp.

- Berger, K. and Schroeder, P., 2012. The Hydrologic Evaluation of Landfill Performance (HELP) Model. User's Guide for HELP-D (Version 3.9 D). 5th, completely revised edition for HELP 3.9 D. Institute of Soil Science, University of Hamburg, Germany, 70 pp.
- Bosbach, D., Bottle, M., and Merz, V., 2010. Experimental study on  $Ra^{2+}$  uptake by barite: Kinetics of solid solution formation via  $BaSO_4$  dissolution and  $Ra_xBa_{1-x}SO_4$  (re)precipitation. Technical Report TR-10-43. Svensk Kärnbränslehantering AB, (SKB), Swedish Nuclear Fuel and Waste Management Co. Stockholm. 106 pp.
- Bruno, J., Bosbach, D., Kulik, D., and Navrotsky, A., 2007. Chemical thermodynamics of solid solutions of interest in nuclear waste management: A state-of-the-art report. OECD Publication Nuclear Energy Agency Data Bank, Eds, OECD Publications Paris, France. 266 p.
- Dixon, K.L., Lee, P.L. and Flach, G.P., 2008. A graded approach to flow and transport modeling to support decommissioning activities at the Savannah River site. *Health Phys* 94(5 Suppl 2): S56-61. doi: 10.1097/01.HP.0000300756.69761.1e. May.
- Doerner, H.A. and Hoskins, W.M., 1925. Co-precipitation of radium and barium sulfates. *J. Am. Chem. Soc.*, 47, 662–675.
- Dong, W., and Brooks, S.C., 2006. Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ , and  $Ba^{2+}$ ) using anion exchange method. *Environ. Sci. Technol.* vol. 40, p. 4689-4695.
- Dong, W., and Brooks, S.C., 2008. Formation of aqueous  $MgUO_2(CO_3)_3^{2-}$  complex and uranium anion exchange mechanism onto an exchange resin. *Environ. Sci. Technol.* vol. 42, p. 1979-1983.
- Duro, L., Grive, M., Cera, E., and Bruno, J., 2006. Update of a thermodynamic database for radionuclides to assist solubility limits calculation for performance assessment. Technical Report TR-06-17. Svensk Kärnbränslehantering AB, (SKB), Swedish Nuclear Fuel and Waste Management Co. Stockholm. 120 pp.
- Dzombak, D.A., and Morel, F.M.M., 1990. Surface complexation modeling - hydrous ferric oxide: New York, John Wiley and Sons, 393 p.
- Engineering Management Support, Inc. (EMSI), 2000. Remedial Investigation Report West Lake Landfill Operable Unit -1. Prepared for West Lake OU-1 Respondents Group. April 10, 2000.
- Engineering Management Support, Inc. (EMSI), 2011. Supplemental Feasibility Study, Radiological-Impacted Material Excavation Alternatives Analysis, West Lake Landfill Operable Unit-1. Prepared for The United States Environmental Protection Agency Region VII, Prepared on behalf of The West Lake Landfill OU-1 Respondents. Prepared in association with Feezor Engineering, Inc. and Auxier & Associates, Inc. December 28, 2011.
- Grandia, F., Merino, J. and Bruno, J., 2008. Assessment of the radium-barium co-precipitation and its potential influence on the solubility of Ra in the near-field. Technical Report TR-08-07. Svensk Kärnbränslehantering AB, (SKB), Swedish Nuclear Fuel and Waste Management Co. Stockholm. 48 pp.
- Guillaumont, R., Fanghanel, T., Neck, V., Fuger, J., Palmer, D., Grenthe, I., and Rand, M. H., 2003. Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium; Elsevier B.V. Amsterdam. 960 p.
- Jacques, D. and Simunek, J., 2005. User Manual of the Multicomponent Variably-Saturated Flow and Transport Model HP1. SCK-CEN Waste and Disposal Department. Belgium, SCK-CEN-BLG-998.

- Langmuir, D. 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. Cosmochim. Acta.* 42:547-569. Mahoney, J.J., 1998. Incorporation of coprecipitation reactions in predictive geochemical models: *in* Proceedings of Tailings and Mine Waste '98, Fort Collins, Colorado, p.689-697.
- Mahoney, J.J., 2001. Coprecipitation reactions – verification of computational methods in geochemical models: *in* Mining Impacted Pit Lakes 2000 Workshop Proceedings: a Multimedia CD Presentation. (Workshop held April 4–6, 2000 Reno, NV). United States Environmental Protection Agency Office of Research and Development. EPA/625/C-00/004.
- Mahoney, J.J., Cadle, S.A. and Jakubowski, R.T., 2009a. Uranyl adsorption onto hydrous ferric oxide – a re-evaluation for the diffuse layer model database. *Environ. Sci. and Technol.* vol. 43, no. 24, p. 9260-9266. DOI 10.1021/es901586w.
- Mahoney, J.J., Jakubowski, R.T. and Cadle, S.A., 2009b. Corrections to the diffuse layer model database for uranyl adsorption onto hydrous ferric oxide - Ramifications for solute transport modeling. Poster presentation at U2009 Global Uranium Symposium, May 2009 Keystone, Colorado.
- Nuclear Energy Agency, Organization of Economic Co-operation and Development (NEA, OECD), 2000. Features, Events and Processes (FEPs) for Geologic Disposal of Radioactive Waste: An International Database.
- Pabalan, R.T., Turner, D.R., Bertetti, P., and Prikryl, J.D., 1998. Uranium VI sorption onto selected mineral surfaces. *in* Adsorption of Metals by Geomedia variables, Mechanisms, and Model Applications. E. Jenne, Editor, Academic Press, San Diego, pp. 99-130.
- Parkhurst, D.L., and Appelo, C.A.J., 1999. User's guide to *PHREEQE* (version 2) - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigation Report 99-4259, 312 p.
- Rand, M., Fuger, J., Grenthe, I., Neck, V. and Rai, D., 2008. Chemical thermodynamics of thorium. OECD Nuclear Energy Agency Data Bank, Eds., OECD Publications, Paris, France. 900 p.
- Rajo, I., Seco, F., Roriva, M., Gimenez, J., Cervantes, G., Marti, V., and de Pablo, J., 2008. Thorium sorption onto magnetite and ferrihydrite in acidic conditions. *Journal of Nuclear Materials*, Vol. 383. Issue 2., p 474-478.
- Sandia National Laboratories. 2010. Features, Events, and Processes (FEPs) for Nuclear Waste Repository Systems. Presentation by Geoff Freeze, Sandia National Laboratories, Albuquerque, NM on July 21, 2010. Presentation accessed on following website on 03-11-2013: [http://www.sandia.gov/IAEA/Presentations/2010/G\\_Freeze\\_SAND2010\\_3348P.pdf](http://www.sandia.gov/IAEA/Presentations/2010/G_Freeze_SAND2010_3348P.pdf).
- Schroeder, P. R., Aziz, N. M., Lloyd, C. M. and Zappi, P. A., 1994a. The Hydrologic Evaluation of Landfill Performance (HELP) Model: User's Guide for Version 3. EPA/600/R-94/168a, September 1994. U.S. Environmental Protection Agency Office of Research and Development, Washington, DC.
- Schroeder, P. R., Dozier, T.S., Zappi, P. A., McEnroe, B. M., Sjostrom, J.W., and Peyton, R. L., 1994b. The Hydrologic Evaluation of Landfill Performance (HELP) Model: Engineering Documentation for Version 3. EPA/600/R-94/168b, September 1994. U.S. Environmental Protection Agency Office of Research and Development, Washington, DC.
- Simunek, J., Sejna, M., and van Genuchten, m. Th., 1998. The Hydrus 1-D Software Package for Simulating the One-Dimensional Movement of Water, Heat, and Multiple Solutes in Variably-Saturated Media – Version 2.0. U.S. Salinity Laboratory, Riverside, California

- Tokunaga, T.K., Kim, Y., and Wan, J., 2009. Potential remediation approach for uranium-contaminated groundwaters through potassium uranyl vanadate precipitation. *Environ. Sci. and Technol.* vol. 43, p. 5467-5471.
- United States Environmental Protection Agency (USEPA), 1996. Soil Screening Guidance: Technical Background Document. EPA/540/R95/128, Office of Solid Waste and Emergency Response (OSWER), Washington, D.C., May 1996.
- United States Environmental Protection Agency (USEPA), 2002. Guidance for Quality Assurance Project Plans for Modeling. EPA/240/R-02/007. December 2002.
- United States Environmental Protection Agency (USEPA), 2008. Record of Decision – West Lake Landfill Site, Bridgeton, Missouri, Operable Unit 1, May 2008.
- United States Environmental Protection Agency (USEPA), 2009. Guidance on the Development, Evaluation, and Application of Environmental Models. EPA/100/K-09/003. March 2009.
- United States Environmental Protection Agency (USEPA), 2012. Personal communication (letter to William Beck and Jessica Merrigan, Lathrop and Gage LLP, Kansas City, Missouri, dated October 12, 2012, regarding Administrative Order on Consent, EPA Docket No. VII-93-F-0005). United States Environmental Protection Agency, Region 7, Lenexa, KS.
- Yoshida, Y., Yoshikawa, H. and Nakanishi, T., 2008. Partition coefficients of Ra and Ba in calcite. *Geochemical Journal*. Vol. 42 pp. 295-304.
- Zhu, C., 2004a. Coprecipitation in the barite isostructural family: 1 Binary mixing properties. *Geochimica et Cosmochimica Acta*, vol. 68, p. 3327 -3337.
- Zhu, C., 2004b. Coprecipitation in the barite isostructural family: 2 Numerical simulations of reactions and mass transport. *Geochimica et Cosmochimica Acta*, vol. 68, p. 3338 – 3349.